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Competing Electron-Electron/Electron-Phonon Interactions And Polyacetylene.

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Abstract. Using Lanczos exact diagonalization, we investigate the effects of the competition between the electron-electron and electron-phonon interactions in the context of the 1-D tight-binding Peierls-Hubbard Hamiltonian, studying various structural, optical, and vibrational properties of strongly correlated systems. We use polyacetylene as our experimental guide, and perform a parameter space search to determine the level at which a unique set of parameters can model this prototypical conducting polymer and, more generally, the applicability of the "simple" 1-D Peierls-Hubbard Hamiltonian to these highly interesting materials.

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1 Introduction

As should be obvious from the other contributions to this conference, amazing progress has been made toward achieving robust, metallic polymers, despite the "theorem" of Peierls that there are no one-dimensional conductors. The theoretical progress has not been as dramatic, and indeed one conclusion from this conference was that there is no consensus as to the nature of the metal/insulator transition, or the nature of the carriers in the metallic phase, for most of the conducting polymers. Similarly, there is little theoretical guidance for design of good non-linear-optical organic materials. The work described here is not an effort to tackle those difficult questions, but rather an attempt to check whether we are starting from the right theoretical viewpoint. We feel this verification of the 1-D PHH as the starting point for gaining a theoretical understanding of conductivity and non-linear optical properties of polyacetylene is necessary. If one is not sure that the competing electron-electron and electron-phonon interactions are modeled properly for simple properties, one cannot hope to calculate more complex quantities with any degree of confidence in the results.

An understanding of the insulating and lightly doped phases of polyacetylene, $(CH)_x$, has been obtained using the simple 1-D Peierls-Hubbard tight-

binding Hamiltonian (PHH), which one hopes models the most important effects of the competition between the electron-electron and electron-phonon interactions. Since this same competition is of importance in many other novel low-D materials of recent interest – e.g., high-temperature superconducting copper oxides, “heavy-fermion” and charge-density wave systems, halogen-bridged transition-metal linear chain complexes (MX chains), and versions of the PHH are commonly used to describe these materials, we feel that the studies here are relevant to the question of the validity of this PHH modeling for the entire class of novel, low-dimensional materials. We have chosen to focus on $(\text{CH})_x$ as it has the simplest (idealized) structure. Thus the prospects of modeling (and understanding) it within the geometrically and quantum chemically simple (single chain, single molecular orbital, nearest neighbor, tight-binding) PHH are greatest. Nonetheless, the correct parameters for modeling $(\text{CH})_x$ remain a matter of much debate [1]. We examine here the question whether this Hamiltonian really can model this prototypical conducting polymer by (1) performing a parameter space search to determine possible parameters and (2) for these parameters, determining the level of agreement between calculated values and several structural, optical, and vibrational properties. Finally, we examine whether these parameters are consistent with those deduced for the finite polyenes by the same methods.

2 Model and Method

In the context appropriate to $(\text{CH})_x$, the PHH takes the form [1]

$$H = \sum_{\ell} (-t_0 + \alpha \Delta_{\ell}) B_{\ell, \ell+1} + \frac{1}{2} K \sum_{\ell} \Delta_{\ell}^2 + U \sum_{\ell} n_{\ell \uparrow} n_{\ell \downarrow} + V \sum_{\ell} n_{\ell} n_{\ell+1} . \quad (1)$$

Here $c_{\ell \sigma}^{\dagger}$ creates an electron in the Wannier orbital at site ℓ with spin σ ; $B_{\ell, \ell+1} = \sum_{\sigma} (c_{\ell \sigma}^{\dagger} c_{\ell+1 \sigma} + c_{\ell+1 \sigma}^{\dagger} c_{\ell \sigma})$; $n_{\ell, \sigma} = c_{\ell \sigma}^{\dagger} c_{\ell \sigma}$; t_0 is the hopping integral with α the e-p coupling describing its distance dependence; $\Delta_{\ell} = y_{\ell+1} - y_{\ell}$ where y_{ℓ} is the (adiabatic) displacement of the ℓ -th CH unit along the axis; and K represents all other costs of distorting the lattice. Coulomb repulsions among electrons are parameterized with the conventional Hubbard U and V .

For the PHH at $1/2$ -filling, it is well known that Hartree-Fock (HF) results are unreliable. Thus we use the Lanczos exact diagonalization method (LEDN) to investigate the effects of competing e-p and e-e interactions on small systems (size $N \leq 16$) and extrapolate to $N \rightarrow \infty$. We have discussed in an earlier “progress report” [2] of this research the size and boundary condition (BC) dependence of results obtained using LEDN. The importance of the Jahn-Teller/non-Jahn-Teller (JT/nJT) distinction for small N is familiar from the finite cyclic polyenes, where $4N+2$ rings do not dimerize; benzene, e.g., has equal bond lengths. This JT/nJT dichotomy becomes a problem when extrapolating

to the infinite $(\text{CH})_x$ limit. For $U=V=0$, one can show that “complex-phase-averaging” [2] – Bloch’s theorem – *exactly* reproduces the long chain behavior from studying short chains with different BCs, but it becomes ineffective in the strongly correlated ($U \rightarrow \infty$) limit for the 1/2-filled band systems currently considered. In this limit, an *amplitude* BC averaging technique has been found to be effective in reducing finite size effects and improving extrapolation to the infinite limit [2].

Within the LEDM scheme, one can calculate several quantities of interest. The value of Δ_ℓ is found by minimizing the total energy. At fixed K , we use the LEDM iteratively to calculate Δ_ℓ from the self-consistency condition (SCC) $K\Delta_\ell = -\alpha \langle B_{\ell,\ell+1} \rangle$. For $\Delta_\ell = a_0 + (-1)^\ell \Delta$, one can reverse the question and consider instead Δ as the independent variable, K (and a_0) then being determined from the SCC. This procedure fails, of course, when $\Delta=0$. Except where we specifically consider defects, we enforce uniform Δ since (1) for parameter space searches, this greatly reduces the computation, as no iteration is needed, (2) this avoids “chain end effects” when extrapolating to the infinite $(\text{CH})_x$ limit, and (3) this agrees with structural data on finite polyenes [3]. While for strong e-p coupling Δ is reduced by U , it is well known that the Hubbard U counterintuitively initially increases Δ for weak e-p coupling [4]. Equivalently, for small fixed Δ , U initially increases K . Phase-averaging yields this behavior on system as small as 8 sites [2], whereas any single BC yields this behavior only after (considerable) extrapolation. Further, the value at 12 sites is nearly converged to the value inferred for the infinite case [2]. Thus BC averaging eliminates many of the problems in applying the LEDM to extract infinite system behavior.

To calculate the phonon dispersion relation, we need to evaluate the dynamical matrix $D_{\ell,\ell'} = \partial^2 E / \partial y_\ell \partial y_{\ell'}$. Here we are interested primarily in the LO ($q=0$ longitudinal optical) mode of the uniform ground state, and thus we need only evaluate the total energy $E[\Delta]$ at three different Δ near the equilibrium geometry, requiring minimal additional computation [2]. Studying only the LO mode has the further advantage that it can be calculated for non-equilibrium geometries, such as enforced uniform Δ . Our studies [2] at fixed K show that for the finite rings ω_{LO}^2 goes soft at finite U , confirming the fact that Δ vanishes at this U , and that finite systems do have a “phase transition” to an AF-SDW state. In general, ω_{LO}^2 tracks Δ [2].

The problem of calculating the optical absorption coefficient within the LEDM reduces to finding the spectral weight of $J_q|\psi_0\rangle$, where J_q is the current operator [2,5].

$$J_q = \frac{i}{\sqrt{N}} \sum_\ell e^{-iq(\ell+1/2)} (t_0 - \alpha \Delta_\ell) \sum_\sigma (c_{\ell+1,\sigma}^\dagger c_{\ell,\sigma} - c_{\ell,\sigma}^\dagger c_{\ell+1,\sigma}), \quad (2)$$

and using the Golden Rule. For small systems, the optical spectra will be sparse. Indeed, benzene has only a single $\pi \rightarrow \pi^*$ absorption. Benzene also illustrates the difference between real rings, where $q=2\pi/N$ corresponds to the physical

current, and “periodic BC’s” which assumes $q=0$ and predicts 2 absorption peaks. BC averaging yields non-sparse spectra as in the infinite system which agree with expectations based on strong- and weak-coupling arguments [2,5].

3 Determination of Polyacetylene Parameters

To begin our discussion, it is useful to recall how the parameters are determined in the conventional SSH model [6] of $(\text{CH})_x$, which corresponds to Eq. (1) with $U=V=0$. Since this is a single-electron theory, it can be solved analytically for the ground state. One finds that the bandwidth is given by $W=4t_0$, the optical gap by $E_g=4\alpha\Delta$, and that the dimerization Δ is determined by the SCC $\pi k=2(K'(\delta)-E'(\delta))/(1-\delta^2)$, where $\delta=\alpha\Delta/t_0$, $k=Kt_0/2\alpha^2$, and E' and K' are elliptic integrals. Fitting to $W=10\text{eV}$, $E_g=1.4\text{eV}$, and $\Delta=0.086\text{\AA}$ yields $t_0=2.5\text{eV}$, $\alpha=4.1\text{eV/\AA}$, and $K=21\text{eV/\AA}^2$. However, $U=0$ parameters can never reproduce the experimental fact that the 2^1A_g state lies below the 1^1B_u state [3], and finite α is required if dimerization is to occur at all. Thus the observed optical gap must come from both e-e and e-p interactions, and hence this investigation using LEDM.

Our LEDM studies [2] suggest that BC averaging on small systems provides reasonable estimates of the infinite limit. Hence one can use manageable size systems to carry out an exhaustive parameter search. Our procedure is to span the dimensionless parameter space: $t_d\equiv 0.5$, $\alpha_d\equiv 0.5$, δ , $u=U/2t_0$, and $v=V/2t_0$; determining k , $e_g=E_g/2t_0$, $w=W/2t_0$, and $\Omega_{LO}^2=\omega_{LO}^2/(4K/M)$. To date for $N=6,8,10,12$ and $x=-1,0,1$, a search over $\delta=.02,.04,\dots,.20$, $v=0,.2,\dots,2.$, and $u=v,v+.2,\dots,3.$, determining ground state properties only, has been completed. K was determined by averaging nJT and chain BCs. The optical gap was defined to be the lowest value of e_g for the 3 BCs (usually JT), and appeared to scale for small V with $U-V$, as predicted by strong-coupling [7]. For $U\simeq 2V$, the gap appeared to depend on $U-2V$ as expected from decoupled dimer arguments [2]. The LEDM does not reliably give outer band edges (nor does experiment); thus w was determined by where the absorption had fallen to 1% of its maximum. Note this can differ considerably from the actual band edge. We found e_g and w had only weak system size dependence at fixed Δ . One also finds w/e_g and Ω_{LO}^2 are remarkably insensitive to parameters.

To determine the parameters describing $(\text{CH})_x$, one then scales each of these dimensionless data points to the actual gap and dimerization to determine the dimensional parameters. If the bandwidth and ω_{LO}^2 then agree with their actual values, one accepts these as possible parameters. However, for $(\text{CH})_x$, even some relatively basic information is not known precisely. For example, although SSH used $\Delta=0.086\text{\AA}$ for the alternating component of the dimerization along the chain, some structural data [8] suggest values as low as 0.022\AA . Also, the appropriate value of the bandwidth W is unclear, as experimental spectra never cutoff cleanly. It is “generally agreed” that $\Delta=0.03\text{\AA}$, $W=10\text{eV}$, and $E_g=1.8\text{eV}$

Table 1: Representative parameters scaled to $\Delta=0.03\text{\AA}$, $W=10\text{eV}$, $E_g=1.8\text{eV}$, and $\tilde{\nu}_{LO}=1450\text{cm}^{-1}$, to fit polycetylene.

N	$t_0(\text{eV})$	$\alpha(\text{eV}/\text{\AA})$	$U(\text{eV})$	$V(\text{eV})$	$K(\text{eV})$	$W(\text{eV})$
8	1.951	5.015	4.683	0.000	56.6	16.1
	1.323	3.911	4.233	0.000	49.4	11.3
	0.950	3.300	3.799	0.000	44.1	8.8
10	1.798	4.953	4.314	0.000	56.4	14.5
	1.477	4.408	4.135	0.000	53.8	12.3
	0.950	3.300	3.799	0.000	44.1	8.8
	0.919	3.283	3.675	0.367	45.9	8.1
	1.099	3.305	4.394	1.318	47.0	8.1
	1.059	2.912	5.933	2.543	43.3	10.6
	1.544	4.333	4.324	0.618	53.6	11.4
	1.796	4.477	5.029	1.437	54.1	12.2
12	1.951	5.015	4.683	0.000	56.6	16.1
	1.595	4.384	4.465	0.000	52.6	13.6
	1.114	3.546	4.012	0.000	46.2	9.9
	0.958	3.194	3.830	0.383	43.9	8.6
	1.121	3.146	4.484	1.345	44.6	8.3
	1.174	2.934	5.634	2.348	42.8	10.6
	1.347	3.788	4.310	0.539	49.0	10.6
	1.869	4.383	5.232	1.495	53.5	14.7

are the values to use. The vibration spectra of $(\text{CH})_x$ is complicated by the zig-zag geometry. Though it has an appreciable isotope effect indicating considerable C-H stretch mixing, the C=C stretch at $\tilde{\nu}_{LO}=\omega_{LO}/(2\pi c)=1450\text{cm}^{-1}$ in $(\text{CH})_x$ is considered to be the mode corresponding most closely to the single LO mode of the theoretical 1D chain [9]. Listed in Table 1 are our results to date for the possible parameters describing $(\text{CH})_x$. We find $t_0 < 2.0$, as part of the bandwidth comes from the electron-electron correlations (U and V). In Ref. 2 we showed, however, that even for a parameter set far from the "conventional wisdom", we obtain optical absorption data, to the extent that they can correctly be determined by the LEDM for non-uniform geometries, in agreement with experiment.

4 Conclusions and Open Issues

LEDM with BC averaging enables reasonable extrapolations from small systems, for which an exhaustive parameter search can be carried in reasonable time. Our current estimates of the parameters modeling $(\text{CH})_x$ are shown in the Table 1. Clearly much work remains. The parameter search needs to be repeated on

Table 2: Representative parameters scaled to $\Delta=0.035\text{\AA}$, $E_g=3.9\text{eV}$, and $\bar{\nu}_{LO}=1605\text{cm}^{-1}$, to fit octatetraene [3]. Chain boundary condition results were used.

N	$t_0(\text{eV})$	$\alpha(\text{eV}/\text{\AA})$	$U(\text{eV})$	$V(\text{eV})$	$K(\text{eV})$	$W(\text{eV})$
8	1.843	2.956	6.637	0.000	37.5	15.0
	1.464	3.146	6.442	0.000	39.3	12.9
	0.994	3.484	5.961	0.000	42.0	10.7
	1.007	3.334	6.040	0.403	41.5	10.4
	1.147	3.079	6.423	0.918	40.0	10.6

Table 3: 2^1A_g and 1^1B_u energies and frequencies for a preliminary “octatetraene” parameter set, $t_0=1.1$, $\alpha=3.2$, $U=6.0$, $V=0.5$, $K=41.0$, inferred from comparing Table 1 and Table 2. The ordering of the states and frequencies agree with experiment [3]. However, the magnitudes do not.

	2^1A_g		1^1B_u	
	$E(\text{eV})$	$\nu(\text{cm}^{-1})$	$E(\text{eV})$	$\nu(\text{cm}^{-1})$
Expt [3]	3.5	1753	3.9	1640
Theory	1.2	1824	3.9	1744

larger systems and the allowed parameters ranges further refined. Dependences of the inferred parameters on experimental inputs need to be understood, and a prescription for defining the bandwidth needs to be agreed upon. The amplitude mode formalism for analyzing the LO mode should also be incorporated. The triplet ($T=1.4\text{eV}$), neutral ($S^0 \simeq E_g$), and charged ($S^\pm = .6\text{eV}$) soliton optical and infrared absorptions have also been identified. Studies of how well the inferred parameters match these data on non-uniform geometries – *i.e.*, whether the same parameters can be used for a microscopic description of the non-linear excitations – are currently underway. Since intrinsic defects can be viewed as $1/N$ effects, extrapolation to large systems may prove very difficult.

Finally, detailed comparisons to finite polyene data, incorporating end group effects as necessary, need to be carried out. If the adiabatic PHH does indeed capture the essential physics, the same parameters should also work for the finite polyenes. Our preliminary studies (see Table 2) indicate that indeed one can fit octatetraene with parameters similar to those deduced above for polyacetylene, although the K is somewhat smaller and t_0 and U somewhat larger than most of the values which are allowed by our polyacetylene search. This is not too surprising, since one expects the finite systems to be more delocalized, and no system size dependence was allowed for K , t_0 , or U (though t_0 has some size dependence through α and the N -dependence of the lattice constant a_0). Certainly the discrepancy is not large, and the fit invalidates the ($U = 0$)

assertion that t_0 "must" be 2.5eV or larger to fit the finite polyene data. We list in Table 3 the values for the (unrelaxed) 2^1A_g and 1^1B_u states for one set of octatetraene parameters from Table 2 in comparison with the experimental values. For this preliminary analysis, we are encouraged by the level of agreement.

Although this research is in progress, it seems that, for $(CH)_x$, the above results confirm that the PHH captures the essential behavior of the competing e-e and e-p interactions and internal consistency can be obtained at the $\simeq 10\%$ level without incorporating further terms into the Hamiltonian. We hope that the lessons and techniques reported here will help lead to a more general microscopic understanding of novel low-D materials with strong competitions for broken-symmetry ground states.

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